REPORT DOCUMENTATION PAGE

1. REPORT DATE (DD-MM-YYYY) 12-07-2007	2. REPORT TYPE Journal Article	3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE **Cation-Cation π-π Stacking in Small Ionic Clusters of 1,2,4-Triazolium (Preprint)**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S) Hui Li (Univ. of Nebraska-Lincoln); Jerry A. Boatz (AFRL/PRSP); Mark S. Gordon (Iowa State Univ.)	5d. PROJECT NUMBER 23030423
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRSP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680	8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-PR-ED-JA-2007-366

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-70448	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-JA-2007-366

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA# 07299A)

13. SUPPLEMENTARY NOTES
Submitted for publication in the Journal of Chemical Physics.

14. ABSTRACT

Aromatic cations such as imidazolium and its derivatives have delocalized charges and, therefore, are often used to synthesize functional nanomaterials, low-melting salts and ionic liquids[1]. Recently, energetic low-melting salts and ionic liquids based on triazolium and its derivatives have received considerable attention[2-4]. A characteristic property of aromatic compounds is their ability to form π-π stacking structures, which can have significant influence on properties. Cation-cation π-π stacking structures are less common, but have been observed in organometallic crystals[5] and imidazolium salts[6]. Cation-cation π-π stacking dimers can be formed in a dielectric solvent due to significant screening of the charge-charge repulsion forces.[7] However, such species in small clusters have not been reported. Calculations reported in this work suggest that cation-cation π-π stacking structures can be formed between two 1,2,4-triazolium cations in small clusters of the two cations and two anions.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Dr. Scott Shackelford
a. REPORT **Unclassified**	b. ABSTRACT **Unclassified**	c. THIS PAGE **Unclassified**	SAR	4	19b. TELEPHONE NUMBER (include area code) N/A

Cation-cation π-π stacking in small ionic clusters of 1,2,4-triazolium (PREPRINT)

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Aromatic cations such as imidazolium and its derivatives have delocalized charges and, therefore, are often used to synthesize functional nanomaterials, low-melting salts and ionic liquids[1]. Recently, energetic low-melting salts and ionic liquids based on triazolium and its derivatives have received considerable attention[2-4]. A characteristic property of aromatic compounds is their ability to form π-π stacking structures, which can have significant influence on properties. Cation-cation π-π stacking structures are less common, but have been observed in organometallic crystals[5] and imidazolium salts[6]. Cation-cation π-π stacking dimers can be formed in a dielectric solvent due to significant screening of the charge-charge repulsion forces.[7] However, such species in small clusters have not been reported. Calculations reported in this work suggest that cation-cation π-π stacking structures can be formed between two 1,2,4-triazolium cations in small clusters of the two cations and two anions.

The *ab initio* calculations were performed with the electronic structure package GAMESS [8,9]. Geometries were optimized using second order perturbation theory (MP2) [10-12] with the aug-cc-pVDZ[13] basis set. Single point energies were calculated for selected structures using MP2 with the cc-pVDZ, aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets[13], and coupled cluster singles, doubles with perturbative triples [CCSD(T)] [14-17] with the cc-pVDZ and aug-cc-pVDZ basis sets.
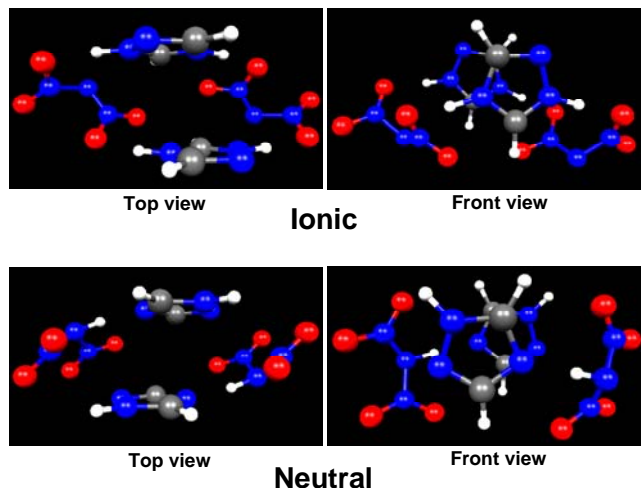

Figure 1. MP2/aug-cc-pVDZ optimized structures of two pairs of 1,2,4-triazolium (1,2,4-triazole) and dinitramide (dinitramine) molecules. H is white, C is gray, O is red, N is blue.

Numerous structures can be found for two pairs of 1,2,4-triazolium and dinitramide ions or two pairs of 1,2,4-triazole and dinitramine neutral molecules. An extensive geometry search was performed for the ionic and neutral structures. The lowest energy MP2/aug-cc-pVDZ structures are shown in Figure 1. In the most stable ionic two-pair structure, each 1,2,4-triazolium forms two hydrogen bonds, via the hydrogens on the N atoms, to the O atoms of the dinitramide ions. Interestingly, this structure exhibits π-π stacking of the two cationic 1,2,4-triazolium rings. The interplane distance is ~3.2 Å, with a parallel displacement of ~1.4 Å. The nitro groups of the dinitramide ions are approximately perpendicular to each other. In the most stable neutral two-pair structure, each 1,2,4-triazole forms one N-H-N hydrogen bond to a dinitramine. There is π-π stacking between the two approximately parallel 1,2,4-triazole rings, with an interplane distance of ~3.2 Å and a parallel displacement of ~1.4 Å. An ionic structure was created from the neutral structure by repositioning protons onto the 1,2,4-triazole molecules. Upon geometry optimization, the protons transfer back to the dinitramide ions to form neutral pairs with no energy barrier.

It is of interest to determine the cluster size at which the ion pair structures become more stable than the corresponding neutral pair structures. A previous study predicted that ion pair dimers are typically higher in energy than neutral pair dimers.[4] The MP2/aug-cc-pVDZ energy of the ionic tetramer in Figure 1 is 1.5 kcal/mol *lower* than that of the neutral one. Including zero point energies (ZPE) obtained with MP2/aug-cc-pVDZ harmonic vibrational frequencies, the ionic tetramer is 1.2 kcal/mol lower in energy than that of the neutral one. The MP2 method tends to predict higher energies for ionic species vs. neutral species.[4] Since the computational cost of CCSD(T)/aug-cc-pVDZ energy calculations of these two tetramer structures is prohibitive, these energies were approximated from the MP2/aug-cc-pVDZ energies by estimating the electron correlation energy differences using three independent methods: (1) the differences between the MP2/cc-pVDZ and CCSD(T)/cc-pVDZ energies of the tetramers, (2) the differences between the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ energies of the twelve pairs of dimers in these two tetramers, and (3) the differences between the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ energies of the eight monomers in these two tetramers. Using these three methods, the estimated CCSD(T)/aug-cc-pVDZ energy of the ionic tetramer is lower than that of the neutral tetramer by 6.0, 7.6 and 8.0 kcal/mol, respectively. Including ZPE, these three values become 5.7, 7.3 and 7.7 kcal/mol, respectively. Further corrections for the basis set effects from aug-cc-pVDZ to aug-cc-

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pVTZ and to aug-cc-pVQZ are small. One can therefore conclude that for two pairs of 1,2,4-triazolium and dinitramide, ionic structures are more stable than the corresponding neutral structures.

The driving force for the formation of the unusual cation-cation π-π stacking structure is also very interesting. Geometry optimization of the ionic structure using HF, which does not contain electron correlation, results in an open-book structure in which the two 1,2,4-triazolium planes form a dihedral angle of ~120° (no π-π stacking). Clearly, electron correlation (a major part of the aromatic π-π attraction) in the MP2 method is the driving force for the formation of the cation-cation π-π stacking structure from the open-book non-stacking structure.

The tetramer interaction energy and the six isolated dimer interaction energies of the four monomers in the ionic tetramer structure in Figure 1 were derived by taking the corresponding energy differences between the tetramer and isolated dimers and monomers, with no correction for basis set superposition errors. The same geometries as in the tetramer were used for the isolated dimers and monomers, and the aug-cc-pVDZ basis set was used. Using HF, the tetramer interaction energy is -217.1 kcal/mol; the repulsion energies between the two 1,2,4-triazolium cations and the two dinitramide anions are +77.1 and +52.9 kcal/mol, respectively; the attraction energies between the two cations and two anions are -96.8, -89.3, -89.3, -96.8 kcal/mol (symmetric due to the symmetry of the tetramer structure). The -217.1 kcal/mol tetramer interaction energy is roughly the sum (-242.2 kcal/mol) of the dimer interactions, with a +25.1 kcal/mol difference due to many-body effects. These HF interaction energies are dominated by Coulomb interactions. For example, a Reduced Variational Space[18] analysis of the two 1,2,4-triazolium cations leads to the following terms (in kcal/mol): total = +77.1, Coulomb = +76.9, exchange-repulsion = +4.9, polarization = -3.8, charge transfer = -0.5 and mixing terms -0.4. In general, the driving force for the formation of ionic clusters is the Coulomb attraction between the opposite-charge ions, which is typically much stronger than the repulsion between the same-charge ions.

However, as shown above, additional dispersion attraction due to electron correlation is necessary for the formation of the cationic π-π stacking structure from the (HF) open-book non-stacking structure. The MP2 tetramer interaction energy is -266.7 kcal/mol, 49.6 kcal/mol stronger than the HF one, due to the electron correlation attraction; the MP2 interaction is roughly the sum (-294.5 kcal/mol) of the MP2 dimer interactions, differing by +27.8 kcal/mol due to many-body effects. The CCSD(T) tetramer interaction energy is not available; the sum of the CCSD(T) dimer interactions is -290.9 kcal/mol, very close to the MP2 one. For the two 1,2,4-triazolium cations, the HF, MP2 and CCSD(T) interaction energies are +77.1, +69.3 and +70.4 kcal/mol, respectively; the electron correlation corrections to the HF interaction energy predicted by MP2 and CCSD(T) are -7.8 and -6.7 kcal/mol, respectively.

Based on the structure of two 1,2,4-triazolium - dinitramide ion pairs (Figure 1), an initial structure of two 1,2,4-triazolium - chloride ion pairs was constructed, and then optimized using MP2/aug-cc-pVDZ. In the optimized structure shown in Figure 2, each 1,2,4-triazolium ion forms two N-H-Cl hydrogen bonds. Apparently, π-π stacking of the two cationic 1,2,4-triazolium rings is formed in this structure in spite of the small sizes of the chloride ions. The interplane distance is ~2.9 Å, with a parallel displacement of ~1.0 Å. The structure is not symmetric due to the parallel up/down displacement (front view in Figure 2). Clearly, very strong N-H-Cl hydrogen bonds are formed in this structure so that the four H atoms bend inward. A neutral structure of two

pairs of 1,2,4-triazole and hydrogen chloride (HCl) molecules was constructed starting from the 1,2,4-triazole - dinitramine neutral tetramer in Figure 1, and then optimized with MP2/aug-cc-pVDZ. The neutral structure optimized to the ionic structure shown in Figure 2, with no energy barrier. Again, electron correlation attraction is the driving force for the formation of the π-π stacking structure: HF geometry optimization of the structure leads to a planar structure in which all the atoms are exactly in the same plane.
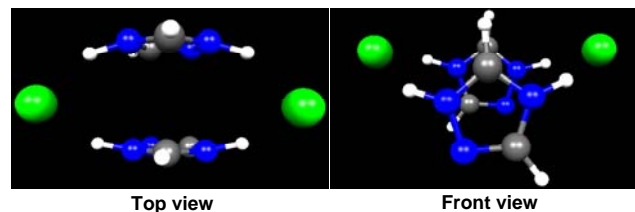

Top view   **Front view**

Figure 2. MP2/aug-cc-pVDZ optimized structures of two pairs of 1,2,4-triazolium chloride ions. H is white, C is gray, N is blue, Cl is green.

In conclusion, *ab initio* calculations suggest that cation-cation π-π stacking structures can exist in very small ionic clusters such as two 1,2,4-triazolium cations and two dinitramide or chloride anions. The structure motifs and interaction patterns found in this study provide new understanding of ionic materials with aromatic rings.

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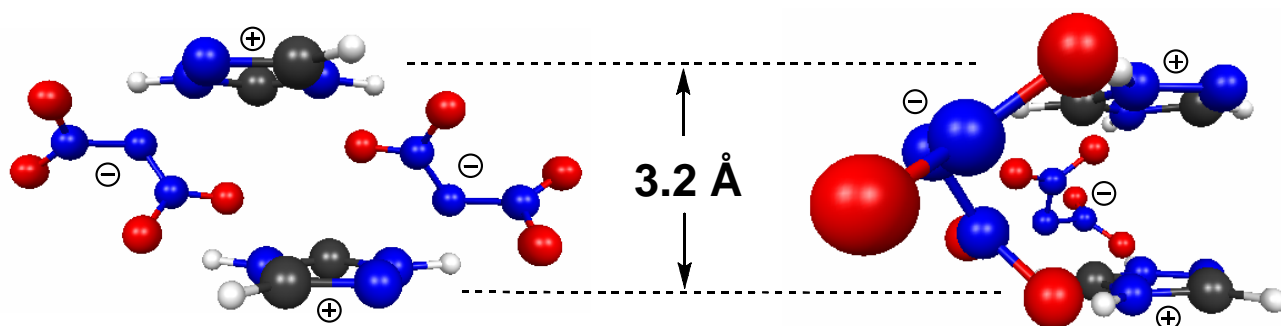
The existence of cation-cation π-π stacking in 1,2,4-triazolium - dinitramide tetramer and 1,2,4-triazolium - chloride tetramer (two cations and two anions) is predicted based on the structures optimized using second order perturbation theory (MP2). In the most stable tetramer structure of 1,2,4-triazolium dinitramide, π-π stacking is formed with an interplane distance of ~3.2 Å and a parallel displacement of ~1.4 Å. In the most stable tetramer structure of 1,2,4-triazolium chloride, π-π stacking is formed with an interplane distance of ~2.9 Å and a parallel displacement of ~1.0 Å.